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UNDERSTANDING METHANOL FORMATION IN PULP MILLS

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ABSTRACT

Methanol emission in pulp mills has been an environmental concern. The Cluster Rule now requires the control of methanol emission in pulp mills. We describe the methanol formation mechanisms during pulping, evaporation of black liquor, and in black liquor storage tanks in this study. We conducted laboratory pulping studies in a batch digester to quantify the methanol formation during pulping. Based on our laboratory experiments, we found that about 75% of the methanol formed in the pulping processes are due to the rapid and completed alkaline hydrolysis reaction of 4-O-methylglucuronic acid residues in hemicellulose (or demethylation of xylan) and lignin demethylation only accounts for less than 20% of the methanol in the spent pulping liquor. We also found from experiments that methanol can be formed during the evaporation of weak black liquor and in the black liquor storage tanks. The methanol formation in these two systems is mainly due to the slow reaction of lignin demethylation. The results indicated that 99% of the methanol including those in the original liquor plus those formed in the evaporation leave the concentrated black liquor after the liquor solids content reaches about 20% and, therefore, can be collected during evaporation. In this paper, we will present the results obtained from our laboratory study along with the implications to mill operations.

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INTRODUCTION

The formation of volatile organic compounds (VOCs), such as methanol, in kraft mills has been an environmental concern. Methanol is soluble in water and can increase the biochemical oxygen demand (BOD). Furthermore, it can also be released into the atmosphere at the process temperatures of kraft mill streams. The cluster rule [1] now requires control of the release of methanol in pulp and paper mills. Unfortunately, knowledge of methanol formation in pulp and paper manufacturing processes is very limited. Methanol is primarily produced through the pulping process in digesters. In a recent study [2], we reported that methanol formation during pulping is mainly due to the rapid demethylation of wood xylan. Recently, many mills have reported that methanol can also be formed in black liquor evaporators and storage tanks. However, the mechanisms of methanol formation in these two systems have not been identified and the amount of methanol formed has not been quantified.

There are two general accepted mechanisms of methanol formation in pulping processes: the hydrolysis of xylan, i.e., the rapid alkaline hydrolysis reaction of 4-O-methylglucuronic acid residues in hemicellulose [3] to form hexeneuronic acid and methanol, and the demethylation of lignin [4, 5]. According to Sarkanen et al. [5], the amount of methoxyl groups on lignin that can be demethylated is very small. Therefore, it is reasonable to assume that the majority of methanol is formed through the demethylation of xylan [3, 5] in pulping. Based on this argument, we conducted a methanol mass balance analysis in our previous study [2] and found that 100% demethylation of xylan accounts for about 75% of the total methanol formed in our laboratory batch pulping processes based on our experimental data. Lignin demethylation accounts for 20% of the total methanol formed. With the assumption of complete hydrolysis of

the xylan methoxyl groups to form methanol in the pulping process, the only pathway for methanol formation from subsequent black liquor processes (storage and evaporation) is by lignin demethylation.

We present some general understanding of methanol formation in pulp mills based on our laboratory studies on methanol formation in pulping, black liquor evaporation, and in black liquor storage. We conducted various laboratory batch pulping processes of different wood species, laboratory batch black liquor evaporation experiments, and investigated the methanol formation in black liquor samples stored in isothermal conditions.

EXPERIMENTAL

Pulping

In a previous study [2] only conventional kraft and soda pulping processes for bleach grade pulps were carried out. In this research, methanol formation in different pulping processes was studied. For each set of pulping conditions selected, the pulping process was terminated at a different pulping time to obtain the rate of formation of methanol and hexeneuronic acid that is directly related to methanol formation through xylan hydrolysis (measured from the pulp only) under a selected set of pulping conditions. By this approach, the effect of pulp kappa number or cooking H factor on methanol formation can be obtained. All the pulping work was conducted in a bomb digester of volume 500 mL. Each cook used 50 grams of oven-dry wood chip. Several pulping processes were carried out. Table I lists the pulping conditions. Methanol concentrations in the pulping spent liquors were analyzed using the method we developed

previously [6] on a commercial Headspace Gas Chromatograph (HSGC, HP-7694 and HP-6890 Hewlett-Packard, Palo Alto, CA).

Black Liquor Storage

As we indicated in the previous section, methanol formation in the post pulping black liquor processes is due to lignin demethylation. To understand methanol formation during black liquor storage, we conducted two sets of experiments. The chemicals used in the first set of experiments were commercial grade softwood lignin and hydroxide solution. Only weak black liquor was used in the second set of experiments. For each set of experiments, the chemicals were put in a sampling vial of volume 20 mL. The vial was heated at various temperatures by an isothermal oven of a commercial Automated Headspace Sampler (HP-7694, Hewlett-Packard, Palo Alto, CA) to simulate black liquor storage process in a constant temperature environment. Multiple headspace extractions from the vial at an interval of 60 minutes were carried out for each sample at a given temperature. The headspace sampler was connected to a GC (described in the previous paragraph) for methanol analysis. It is assumed that the amount of methanol vapor extracted out for GC measurement was very small compared to the total methanol in the liquid because the methanol vapor conentration in the headspace is very low.

Black Liquor Evaporation

Laboratory batch black liquor evaporation experiments were conducted using an isothermal bath. The isothermal bath uses polyethylene glycol (PEG) as heating medium. The flashing point of PEG is 149°C. Figure 1 shows a schematic of the batch evaporator that consists of a homemade boiler of capacity 100 mL, distillation column that was set up vertically to

prevent the overflow of foaming liquor due to heating. The distillation column was heated using a heating tape to prevent condensation on the wall. The vapor was condensed in a graduated cylinder (as a receiver) that is cooled by an ice bath. The volume of the condensate can be easily read from the scale on the cylinder and recorded during experimentation. The temperature of the PEG was controlled using a temperature controller to obtain a constant heat flux to the boiler. The same amount of 50 mL black liquor was used for each batch experiment. Several batch evaporation experiments were carried out. The duration of each batch evaporation was varied to obtain the time dependent methanol formation and vaporization data. It should be noted that the starting liquor composition, solids, etc., are the same as they are taken from the same source. The HSGC described above was used for methanol analysis.

RESULTS

Methanol Formation During Pulping

Based on our previous laboratory pulping study [2], we can conclude that 75% of the methanol was formed during pulping by the 100% hydrolysis of xylan. Lignin demethylation contributes 20% of the methanol formed in pulping. The effects of kappa number of pulping process on methanol formation were studied in this research. We conducted conventional kraft pulping with and without catalyst AQ at two different sulfidities, soda pulping, polysulfide pulping with and without AQ at two different sulfidities, and a multistage pulping to simulate a RDH process. For each pulping process selected, several batch cookings were conducted that were terminated at different cooking times to obtain desired kappa number. Only southern pine was used in the present study. Pulp yield, kappa number, and methanol concentration in the pulping spent liquors were analyzed.

Figure 2 shows the results of methanol formation per ton of oven-dry pulp calculated based on the measured quantities. The results confirmed our previous study [2] that the effect of pulping process and catalyst AQ on total methanol formation is not very significant. The data show that the total methanol formed per ton of oven-dry pulp is a strong function of pulp kappa number or H factor, indicating the effect of ongoing xylan hydrolysis and lignin demethylation reactions on methanol formation. The scatter of data is partly due to the actual small variations of pulping processes and partly due to measurement errors. The fact that the data scatter in Fig. 2b is not as severe as in Fig. 2a indicates that methanol formation reactions (I) and (II) are strongly affected by the cooking H factor (total energy input), or temperature. The data also show that about 8.5 and 7.0 kg/ODT pulp methanol will be formed in the pulping of bleach grade (kappa = 30) and liner board grade (kappa = 70) southern pine, respectively. The fact that the pulping process does not have a significant effect on methanol formation indicates that rapid and complete hydrolysis of xylan is the major pathway for methanol formation, and lignin demethylation does not significantly contribute to methanol formation in pulping. Measurements of hexeneuronic acid (HUA) groups show that the amount of HUA found in pulp was linearly proportional to the methanol concentration in the pulping spent liquor up to 75% of the concentration level, which further validates the above conclusion. For practical application purposes, we conducted a regression analysis to obtain the following equations for the prediction of methanol formation during pulping.

$$m_{MeOH}(kg/ODTPulp) = 10.09 - 0.031 \cdot kappa - 0.00017 \cdot (kappa)^2 \quad (1)$$

$$m_{MeOH}(kg/ODTPulp) = 0.644 \cdot (HFactor)^{0.368} \quad (2)$$

It should be pointed out that the above two equations are simply a mathematical fit of the data. The equations neglect the effects of AQ, sulfidity, and other pulping parameters and were obtained for southern pine only. It is intended for qualitative prediction only. The actual experimental data are needed to be used for accurate applications.

Methanol Formation During Black Liquor Storage

Model System

Laboratory simulation experiments using caustic solution with alkali softwood lignin in an isothermal environment were conducted at several temperatures. Both the lignin and hydroxide concentrations were varied. The results indicate that methanol can be formed through the demethylation of lignin as shown in Fig. 3, though the lignin demethylation is very slow. We also found that the methanol formation is linearly proportional to the lignin mass concentration in the caustic solution as shown in Fig. 4. However, the effect of pH, or the hydroxide concentration on methanol formation is not significant as shown in Fig. 5. Based on the data presented in Figs. 3-5, we obtained the following kinetic expression for qualitative prediction of methanol formation rate in black liquor storage,

$$\frac{dC_{MeOH}}{dt} = Z \cdot \exp\left(-\frac{E}{RT}\right) \cdot (C^0_{lig})^a \cdot (C^0_{OH^-})^b \qquad (3)$$

where Z = 1062.5, E = 2.6822X10^7, a = 1.0, and b =0.1. C^0_{lig} and $C^0_{OH^-}$ are the initial lignin mass and hydroxide mole concentration, respectively.

overall methanol formation from the liquor with low kappa is greater than that from the liquor with high kappa. To explain this phenomenon, we also compared the results from the liquor with pulp kappa = 104 with the data obtained from a model system shown in Fig. 3. The comparison